

B1



Europäisches Patentamt

European Patent Office

Office européen des brevets

(11) Publication number:

0 070 715

B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 18.03.87

(51) Int. Cl. 4: G 03 G 5/082, H 01 L 21/203,
H 01 L 31/18, H 01 L 21/306,
H 01 L 21/318

(71) Application number: 82303757.7

(73) Date of filing: 16.07.82

(54) Glow discharge method and apparatus and photoreceptor devices made therewith.

(86) Priority: 17.07.81 US 284333

(86) Proprietor: PLASMA PHYSICS CORPORATION
Box 548 Locust Valley
Long Island New York 11560 (US)

(45) Date of publication of application:
26.01.83 Bulletin 83/04

(72) Inventor: Coleman, John H.
Box 548
Locust Valley, LI, NY 11560 (US)

(45) Publication of the grant of the patent:
18.03.87 Bulletin 87/12

(74) Representative: Pears, David Ashley et al
REDDIE & GROSE 16 Theobalds Road
London WC1X 8PL (GB)

(44) Designated Contracting States:
DE FR GB NL

(56) References cited:
GB-A-2 018 446
US-A-4 225 222
US-A-4 226 897
US-A-4 265 991

EP 0 070 715 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European patent convention).

Description

The invention relates to photoreceptors for electrophotography disposed upon the surface of an electrically conducting substrate, and to improved photoreceptors which are composed of amorphous silicon having a dielectric layer which increases the voltage which can be applied to the surface (the surface voltage V_s), in the dark, while reducing the residual voltage under illumination.

The photoreceptor utilizing hydrogenated amorphous silicon (a-Si:H) and a dielectric layer described above is an improvement over a photoreceptor described in US-A-4 330 182, a continuation-in-part of US-A4 226 897 in which blocking layers were disclosed.

In the past, prior art devices described in US-A-4 225 222 which issued September 30, 1980, to Kemper described p-n junctions in amorphous silicon for electrophotography. Other amorphous photoreceptors were described by Mort et al in Photographic Science and Engineering, Vol. 24, No. 5, pages 241-250. Also, GB-A-2 018 446 filed on March 2, 1979 by Misumi et al and US-A-4 265 991 which issued May 5, 1981 to Hirai, described blocking layers on imaging-forming members. Other blocking layers on amorphous silicon photoreceptors were described by Shimizu, Komatsu and Inoue in Photographic Science & Engineering, Vol. 24, No. 5, September 1980, in pages 250-254. These blocking layers increased in the dark surface voltage (V_s) but retained substantial surface charge under illumination, thereby reducing voltage contrast.

A photoreceptor according to the present invention is characterised in that a first layer of semiconductor material is disposed upon the surface of the substrate, a dielectric layer is disposed upon the surface of the first layer of semiconducting material, and a second layer of semiconductor material is disposed upon the surface of the dielectric layer, and in that the thickness of the dielectric layer is sufficiently great to increase the surface voltage which can be applied to non-illuminated areas of the surface of the second layer of semiconducting material during corona charging, over that which can be applied to a layer of the semiconducting material alone, and sufficiently small to reduce the charge remaining on areas of the surface of the second layer of semiconducting material when the photoreceptor is illuminated by electromagnetic radiation. The present invention also provides apparatus (defined in claim 5) and a method (defined in claim 10) for producing photoreceptors according to the invention.

Apparatus suitable for making photoreceptors according to the present invention and using asymmetric electrical fields is described in above-mentioned US-A-4 226 897. Suitable apparatus with uniform electrical fields is described in US-A-3 069 283. Improved apparatus is described herein.

In a series of experiments, it was found that when a thin dielectric layer was applied to an

a-Si:H photoreceptor by exposing the a-Si:H to activated species of nitrogen using, for example, the method described in the above mentioned US-A-4 226 897, the dark V_s was increased significantly while the V_s due to residual charge after exposure was reduced to a low value. Although a nitride layer on a-Si:H was found previously to increase the Schottky barrier voltage by a few millivolts, it was found that the increase in V_s was in excess of ten volts and higher when the nitride layer was applied to the surface of an a-Si:H photoreceptor. In the preferred embodiment, it was found that improved photoreceptor properties resulted when a dielectric layer was applied between semiconductor layers. The dielectric layer, when formed whether by activated nitrogen species or by a glow discharge in silane and ammonia, was blocking to charge carriers flowing in the dark, but was substantially conducting to charge carriers generated by electromagnetic radiation analogous to a rectifier. The semiconductor layers used in the experiments included p-doped, n-doped, and intrinsic layers of a-Si:H.

Furthermore, a photoreceptor was produced capable of being charged in either polarity by applying a P-doped a-Si:H layer, a nitride of silicon layer, and an intrinsic layer sequentially to an aluminum drum. When the drum was substituted for a selenium alloy photoreceptor drum in a commercially available electrostatic office copier with liquid toner, high quality image reproduction was attained. The image resolution was exceptionally high since there is no detectable grain in the a-Si:H, and the residual charging was low. Also, other problems were eliminated which are usually associated with photoreceptors, such as, for example, reverse charging when its surface area was brushed to remove toner during the cleaning cycle.

In addition, improved apparatus is described herein which is particularly useful for plasma coating photoreceptor drums and tape during manufacture on a commercial scale.

Thus, one object of the present invention is to increase the dark surface voltage accepted by a photoreceptor composed of a-Si:H. Another object is to reduce the residual charge on an a-Si:H photoreceptor under illumination. Still another object is to provide an improved electro-photographic system. Also an objective is to provide a rectifying barrier in a photoreceptor which blocks charge flowing in the photoreceptor while in the dark, and conducts charge generated under illumination. Finally, another object is to provide a method and apparatus which enables the glow discharge disclosed in US-A-4 225 222 to be maintained at a reduced voltage.

The invention will be described with reference to the drawings, in which:

Fig. 1 is a schematic, cross-sectional view of glow discharge apparatus having a known electrode arrangement for coating cylindrical drums;

Figs. 2, 3 and 4 are cross-sections of three

embodiments of an amorphous silicon photoreceptor made with the apparatus of Fig. 1 in which thicknesses of layers have been exaggerated,

Fig. 5 is a cross-section of an amorphous silicon photoreceptor deposited on a semi-transparent substrate;

Fig. 6 is a cross-section of an electrophotographic copy machine which uses the amorphous silicon photoreceptor of Fig. 3,

Fig. 7 is a cross-section illustrating schematically glow discharge apparatus for simultaneously coating or etching a plurality of cylindrical drums, using a known electrode arrangement;

Fig. 7A shows apparatus according to the invention, for coating or etching a plurality of cylindrical drums,

Fig. 8 is a side view in cross-section illustrating schematically glow discharge apparatus according to the invention for coating planar members, and

Fig. 9 is a cross-sectional view of glow discharge apparatus according to the invention for simultaneously coating or etching a plurality of planar substrates.

Referring to Fig. 1 a glow discharge apparatus is positioned on a header plate 12 which is hermetically sealed to an enclosure 6. A cylindrical drum 1 of aluminium having an outer surface 11 to be coated is supported in the enclosure 6 by a ceramic post 3. Ends discs 2a, b are fitted into the open ends of the cylinder 1. The disc 2b is connected to the centre conductor 13 of the ceramic post 3, which electrically connects the cylinder 1 to the negative terminal of a power supply 10. The ceramic post 3 is hermetically sealed into the header 12. Counter electrodes 4a, b of, for instance, stainless steel tubing, are supported by ceramic posts 19a, b respectively, posts 19a, b being hermetically sealed into the header 12. The center conductors 8a, b of posts 19a, b electrically connect the counter electrodes 4a, b respectively to the positive terminal of the power supply 10 through protective impedances 17a, b respectively. A heating element 9 mounted inside the cylinder 1 is electrically connected through suitable terminals (not shown) to an external power source (not shown). Heating elements 14a, b are mounted inside the counter electrodes 4a, b and are connected through suitable terminals (not shown) in header 12 to an external power source (not shown).

The enclosure 6 may be evacuated by a vacuum pump (not shown) by way of a tube 7, before gases G from gas supply tanks (not shown) are introduced into the enclosure 6 through appropriate valves 16a, b . . . z, via a line 15, hermetically fitted in the header 12, and a second line 5.

In operation, the atmosphere in enclosure 6 is evacuated through tubing 7 to a pressure of about 1.36 mPa (0.1 Torr) or less and the enclosure 6 is back-filled with the desired film-forming gases G. Various coatings may be produced in the apparatus of Fig. 1 such as, for example, the photoreceptor illustrated in Fig. 2.

Referring now to Fig. 2, a substrate surface 21 is coated first with an n-type layer 22 of a a-Si:H using gases G consisting of a mixture of silane (SiH_4) and phosphine (PH_3). The P/Si mixture, which is in the ratio of 0.01% to 1% or greater, is admitted into the line 5 by adjusting the valves 16a, b. The gases G may be diluted, for example, to 5% SiH_4 in He and 1% PH_3 in He and operated in the pressure range of 13.6 to 41.0 mPa (1 to 3 Torr). The temperature of substrate 1 is maintained at 230°C or higher by adjusting the current to heater 9. Counter electrodes 4a, b may be 200°C or higher by adjusting heaters 14a, b to increase the electrical conductivity of the material deposited on the surfaces of counter electrodes 4a, b during deposition which would otherwise impede the flow of current from the plasma to the anodes 4a, b. The layer 22 may be coated to 30 nm and thicker by adjusting voltage V to about 360 volts and maintaining a current density of 0.1 mA/cm² for about one minute or longer.

Next, the phosphine flow valve 16b is closed and the SiH_4 continues to form an intrinsic a-Si:H layer 23 to attain the desired thickness, dependent on the desired operating voltage of the final device. The SiH_4 valve 16a is closed and the enclosure 6 is evacuated. NH_3 is then admitted through the valve 16c to a pressure of about 2.73 mPa (0.2 Torr) and the glow discharge continued for about 30 minutes with power source 10 adjusted to 300 volts and the current I of 0.1 mA/cm² and higher, thereby forming a nitride of silicon layer 24 in a similar manner to that described in the above mentioned U.S. patent no. 4,226,897.

Under test, using a one μm thick a-Si:H layer 23, a surface voltage Vs of -30 volts was produced in the dark using a conventional Corotron corona charger. No positive charging was noted. Without the nitride layer 24, a surface voltage Vs of only about -15 volts was produced with the same thickness of a-Si:H layer 22. Next, under illumination of 0.2 microjoules at 550 nm, the surface voltage Vs of the photoreceptor with the nitride layer 24, decreased to approximately zero. Finally, the drum 1 coated as shown in Fig. 2 was used in a commercially available electrophotographic office copier in place of the conventional selenium drum. When the drum 1 was negatively charged, exposed, and developed with liquid toner by the Carlson method, it produced high quality toned images which transferred to standard paper.

Thus, in the dark, the nitride layer appears to block the flow of holes from the aluminium substrate as well as to block the holes which are generated thermally in the a-Si:H layer from flowing to the surface. Significantly, the charge carriers generated by illumination appear to tunnel through the nitride layer 24 and discharge the Vs to a low value, indicating that the dielectric layer possesses rectification properties.

Referring now to Fig. 3, a photoreceptor is illustrated having a surface 31 of the substrate 1 which, for example, may be the aluminium drum

illustrated in Fig. 1. First, a p⁺ semiconductor layer 32 is deposited on the surface 31 in the apparatus of Fig. 1 having a B/Si ratio preferably in the range of 0.01% to 1% with a thickness range of 30 nm to 1 μm. During deposition the temperature is maintained in the range of 250°C to 450°C. The higher temperatures are preferred initially for best adhesion to the substrate surface 31, after which the temperature is preferably reduced to 250°C. At the higher temperatures, chemical vapour deposition (CVD) was noted to occur by pyrolysis on the substrate surface 31 and, indeed, suitable p⁺ layers 32 were produced at 450°C without applying the glow discharge. A nitride of silicon layer 33 was then produced on the p⁺ layer 32 by a glow discharge in NH₃ for 30 minutes, as described above. Finally, the temperature of the substrate 1 was held at 250°C and an intrinsic a-Si:H layer 34 of about 5 μm thickness was plasma deposited on the nitride layer 33 by a glow discharge in silane, thereby providing layers in the following sequence: Intrinsic a-Si:H/dielectric/p⁺ a-Si:H.

Under test, the photoreceptor illustrated in Fig. 3 with a 5 μm thick intrinsic a-Si:H layer 34 was charged in the dark to a Vs of +80 volts. Surprisingly, the same photoreceptor could be charged in the dark to a Vs of -110 volts. Both polarities of Vs discharged to a few volts under illumination of 2 microjoules at 550 nm. Without the nitride layer 33, Vs on layer 34 charged in the dark to less than +25 volts, and charged negatively to only a few volts. The dielectric layer 33 appears to block charge carriers present in the dark, while to be conducting to charge carriers generated by electromagnetic radiation when charged to either polarity. Thus, the dielectric film has properties analogous to a rectifier, except that the effect is independent of polarity.

Indeed, in a further experiment, a top semi-transparent electrode of Cr was evaporated on the intrinsic a-Si:H layer 34 to form a photodiode structure; and, when an external voltage of 10 volts was applied between the semitransparent electrode and substrate, the current flowing in the dark was less than a microamp, whereas under illumination several millamps were measured.

Next, the gases G containing a mixture of silane and NH₃ were admitted simultaneously during the glow discharge to form a Si_xN_y dielectric film. The discharge was maintained for about 6 minutes to deposit a 100 nm Si_xN_y layer 33 on p layer 32. Similar dark Vs and illuminated discharge values were obtained to those described above when the dielectric layer 33 was produced by discharging in NH₃ alone.

In addition to producing positive and negative charging, the photoreceptor illustrated in Fig. 3 is the preferred embodiment of the invention, since the dielectric layer 33 is positioned between two semiconductor layers and, therefore, dielectric layer 33 is protected from the mechanical wear involved during the toning, image transfer, and cleaning cycles of the Carlson process. Also

under test in a commercial electrophotographic copy machine, high quality images were produced.

Referring to Fig. 4, a p-type layer 42 is applied to the surface 41 of substrate 40, after which a Si_xN_y layer 43 is applied to the surface of layer 42, as described in connection with Fig. 3. An n-type layer 44 in the range of 30 nm to 1 μm thick was applied to the surface of a Si_xN_y layer 43 and an intrinsic a-Si:H layer 45 applied to the layer 44. Thus the photoreceptor had layers in the following sequence: intrinsic a-Si:H/n a-Si:H/dielectric/p a-Si:H/metal substrate.

Under corotron charging, a negative Vs of -20 volts was accepted by a layer 44 of one μm thickness. No positive charging was observed since the negative majority carriers in the n-type layer in layer 44 drift to a positive charge. However, the dielectric layer 43 increased in the Vs by blocking holes from the p-layer and from the substrate 11. Again, there is no residual voltage under illumination since the photo-induced charge carriers appear to tunnel through dielectric layer 42.

Referring to Fig. 5, the substrate 1 is a glass plate 51 with a semi-transparent, conducting-metal-oxide coating 52 composed of, for example, fluorinated tin oxide 150 nm thick. The coating 52 may be coated with a protective layer 53 of 3 nm silicon oxide formed by oxidizing a plasma deposited a-Si:H layer.

Next, with the substrate 1 held at 250°C the layers described in connection with Fig. 3 were applied sequentially to the oxide layer 53; i.e., a p-type a-Si:H layer 54, an nitride layer 55, an intrinsic a-Si:H layer 56.

In operation the photoreceptor illustrated in Fig. 5 charged to Vs of +50 volts and -70 volts in the dark and discharged to a low value under illumination as low as 0.2 microjoules/cm² when the thickness of the intrinsic a-Si:H layer 56 was similar to that described in connection with Fig. 3.

The devices illustrated in Figs. 2—5 were next plasma deposited in the apparatus illustrated in U.S. Patent No. 3,069,283 using a uniform electric field, and similar results were found to those described above. Also, the silane used to produce the intrinsic, n-type, and p-type layers was replaced with the following gases: disilane, fluorosilane, and fluorodisilane. In each case the photoreceptor produced similar results under test to those obtained with silane-He mixture. Also, when the power source 10 illustrated in Fig. 1 was charged to 60 Hz, audio frequencies from 60 to 20 Hz or radio frequencies from 20 Hz to 200 MHz and photoreceptors were produced such as illustrated in Figs. 2—5, similar results were found. Finally, a-Si:H produced by sputtering or evaporating Si in a hydrogen atmosphere gave similar results.

Referring to Fig. 6, a cross-sectional view of an electrostatic copier particularly suited to the present photoreceptor is illustrated schematically. A rotating drum 61 mounted on an appro-

priate shaft moves the a-Si:H photoreceptor 62 produced, for example, as described in connection with Fig. 3. Positioned around the periphery of drum 61 are a corotron charging unit 63, an exposure station 64, a toner development system 65 with its development electrode adjusted to the appropriate potential, a paper transfer station 67 with an appropriate transfer corona 67a, and a cleaning station 66. Paper feed rollers 68 hold the paper 68a against the drum under the transfer corona station 67 as is well known in the art. An erase lamp may be used as illustrated.

In operation with an a-Si:H photoreceptor such as described in connection with Fig. 3, high quality images were obtained with a Vs as low as 80 volts when a typewritten letter was copied onto the surface of the photoreceptor 62. When an insulating Mylar belt was added to the surface of photoreceptor 62 and a corona charger (not shown) was added to the exposure station, good images were obtained for Vs as low as 50 volts.

Next, referring to the exposure station 64, the optics for imaging a page onto photoreceptor 64 were removed and a He-Ne laser (not shown) was installed in the exposure station 64 and raster scanned across the a-Si:H surface 61, while being modulated with an acousto-optic modulator in accordance with a data stream, as is known in the art. Again, high resolution spots or images were transferred to the paper with a conventional treated surface for liquid toner. Both analog images and digital spots were recorded successfully.

Finally, referring to Fig. 7, a cross-sectional view of glow discharge apparatus mounted in enclosure 79 hermetically sealed to header 78 is illustrated schematically. A pair of drums 70a, b to be coated are connected by leads 76a, b respectively to an electrical transformer 77. Electrodes 71a, b alternatively function as anode and cathode during each half cycle of the voltage induced on the transformer 77. The drums 70a, b are supported by shafts 72a, b mounted in bearings (not shown) which are supported on the header plate 78 by insulated blocks 73a, b respectively. The drums 70a, b have surfaces 71a, b to be plasma coated from film-forming gases. The transformer 77 is connected to the drums 70a, b through protective impedances 75a, b and leads 76a, b which may be conveniently connected to the shafts 72a, b respectively through bearings (not shown) or other sliding contacts. Film-forming gases G are introduced as illustrated into the vicinity of drums 70a, b from line 74 and appropriate flow controllers FC and feed tanks (not shown).

The method of operation of the deposition system of Fig. 7 is similar to that of the system of Fig. 1 in that the film forming gases are introduced into the region of the drum surfaces 71a, b through line 74 and flow controllers FC from tanks (not shown), after which the voltage from the transformer 77 is adjusted to maintain a glow-discharge with the desired current density of, or greater than, 0.1 mA/cm^2 and higher. However,

both electrodes 70a, b have substrate surfaces 71a, b to which the coatings are applied on alternate cycles, thereby eliminating the necessity for a counter electrode which otherwise would wastefully collect some deposit. The frequency of the power from a power source (not shown) applied to transformer 77 may be in the range of 60 Hz to 100 MHz with appropriate matching networks. The drums may be rotated by an external motor (not shown) and drive shafts (not shown) to produce a uniform discharge. Although the cathode glow around the drum surface 71a or b connected during its negative half cycle can be adjusted to produce a uniform deposition, the opposing drum 71a or b is anodic for that half cycle, and its deposit occurs on the area closest to the cathode. However, rotation of drums 71a, b then produced uniform coatings.

In tests, all analog and homolog molecules of silane, H_2 , and the halogens were found to produce useful films as well as dopants and other film-forming gases available commercially.

In addition, referring to Fig. 7A it was found that when leads 76a, b electrically connected both the drums 70a, b to the negative terminal of D.C. power supply 180 while the positive terminal was connected to header 78 or metallic gas line 74, an improved glow discharge occurred to the drum surfaces 71a, b. Indeed, when the separation S between the surfaces 71a, b, as designated by "S" in Fig. 7A was varied and the current was maintained constant, the voltage required to sustain the glow discharge decreased when the separation S was adjusted so that the cathode glows above surfaces 71a, b approached one another. Under these conditions less power is required and better film quality in surfaces 71a, b was attained.

In operation, the heaviest deposit was noted to occur in the region of closest separation; however, nonuniformity in thickness was averaged out by rotation of drums 70a, b as shown. Similar results were obtained with a pulsating D.C. supply 180, and with an A.C. or R.F. supply with a negative bias preferably on drums 70a, b.

Finally, referring to Fig. 8, the drums 70a, b illustrated in Fig. 7A were replaced with flat plate substrates 80a, b, having a separation S between opposing surfaces 81a, b. As described above, film forming gases from tanks (not shown) are admitted through flow controllers 82a, b, c, through a line 83 in the header 84 into the vicinity of the substrate surfaces 81a, b. The enclosure 85 is evacuated through the line 86 by a vacuum pump (not shown) as described above. One terminal of a power supply 87 is connected through leads 88a, b to the substrates 80a, b respectively, through protective impedances 89a, b. The other terminal of the power supply 87 is connected to the header or to the gas supply lead 83 which acts as the counter electrode. Heaters 91a, b in the substrates 80a, b are powered by an external power source (not shown) to maintain the desired substrate temperature, or an external source may radiantly heat substrates 80a, b.

In operation, the desired film forming gases such as, for example, silane and its dopants, as described in connection with Fig. 3, are admitted through line 83 into the enclosure 85. The power supply 87 may be pulsating D.C. with the most negative polarity connected through the leads 88a, b to the substrates 80a, b to maintain a glow discharge around substrate surfaces 81a, b. When the separation S is adjusted to position the negative glow regions above surfaces 81a, b in close proximity to one another, the voltage from power source 87 required to maintain the same current was observed to decrease. For example, using 101.6 mm × 203.2 mm (4" × 8") aluminum plate substrates 80a, b and 5% silane in He at 27.3 mPa (2 Torr) pressure, the voltage required to sustain 50 mA decreased from 360 to 340 volts when the separation S was decreased from 50.8 to 25.4 mm (2 inches to 1 inch).

Under test, uniform films with good semiconductor properties were noted. Other gases gave similar results provided the cathode glows on the substrate surfaces were adjusted in close or overlapping proximity. (The effect was useful until the separation S was so small the glow discharge was extinguished). Under such conditions the apparatus illustrated in Fig. 8 was found to deposit improved a-Si:H films from silane, disilane, SiF₄, difluorosilane and various combinations of dopants including hydrogen, fluorine, diborane, phosphine and arsine. Other semiconductor gases found to deposit improved films included germane and trimethyl gallium with arsine.

In addition, when a silicon wafer was placed on the surface 81 of the electrode 80 in the apparatus illustrated in Fig. 8 and the reactive gases that are etchants of Si such as, for example, CH₄ and O₂, were introduced through tube 83, rapid etching of Si, SiO₂ and Si₃N₄ was observed under glow discharge. Also, BC₃ was found to etch Al layers on Si. Introduction O₂ alone was found to form SiO₂ on a Si wafer during a glow discharge and the addition of a few percent of CF₄ enhanced the oxidation rate. Although this etching reaction is similar to that known in the art, the apparatus of Fig. 8 was found to reduce the power required to operate in a stable manner at lower pressures and to produce better anisotropic etching than conventional parallel planar reactors or inductively coupled reactors.

Referring to Fig. 9, a number of substrates 91, such as Si wafers, are held in a conducting tray 92 which is electrically connected to the header 94 and to ground. The header 94 forms a vacuum-tight enclosure with a quartz tube 93 by means of a gasket (not shown). The conducting wafer tray 92 may be cantilevered from the header 94. An IR oven 98 positioned around quartz tube 93 may be used to radiantly heat substrate 91. Gases G are admitted from tanks (not shown) and a flow controller 99 through tubing 96 in the header 94 and past the substrates 91. The reaction by-products of gases G are exhausted through tubing 95 by a vacuum pump (not shown).

To provide an electric field to the substrates 91, a

counter electrode 97 in the form of nickel tubing is mounted on an electrical feed-through 101 in the header 94. The center conductor of the feed-through 101 may be connected to the positive terminal of a power supply 102, the negative terminal of which may be grounded to header 94.

Again, as described in connection with Fig. 7 and Fig. 8, the separation S between substrates 91 is adjusted for the desired pressure of gases G so that the cathode glow regions have juxtaposed surfaces of substrates 91 are in sufficiently close proximity to interact and reduce the voltage required for deposition or etching. The substrates 91 may be of any desired material instead of the Si wafers and gases G may be any mentioned above or others, deposition or etching being determined by the gases G being used. Also, pulsating D.C., A.C., or R.F. power supplies may be used between the substrates 91 and the counter electrode 97, although the enhanced glow discharge only occurs during the portion of the voltage cycles in which substrates 91 are negative relative to counter electrode 97.

In addition to using the well known Carlson method of toning the electrostatic images on the photoreceptors, it was found that by coating the photoreceptors illustrated in Figs. 2-5 with a conventional thermoplastic polymer and then corona charging them, a physical image was produced in the polymer. Specifically, when the photoreceptor was exposed to a light image from, say, a laser beam, the surface charge was selectively discharged. The application of heat to the softening point of the polymer then permitted the portion of the surface which retained charge to physically deform in accordance with the charge pattern. The pattern was then read by a laser, as is known in the art.

Claims

1. A photoreceptor disposed upon the surface of an electrically conducting substrate, characterised in that a first layer (32; 42; 54) of semiconductor material is disposed upon the surface of the substrate (1), a dielectric layer (33; 43; 55) is disposed upon the surface of the first layer of semiconducting material, and a second layer (34; 44; 45; 56) of semiconductor material is disposed upon the surface of the dielectric layer, and in that the thickness of the dielectric layer (33; 43; 55) is sufficiently great to increase the surface voltage which can be applied to non-illuminated areas of the surface of the second (34; 44; 45; 56) layer of semiconducting material during corona charging, over that which can be applied to a layer of the semiconducting material alone, and sufficiently small to reduce the charge remaining on areas of the surface of the second layer of semiconducting material when the photoreceptor is illuminated by electromagnetic radiation.

2. A photoreceptor according to claim 1, further characterised in that the first layer (33; 42; 54) of semiconductor material comprises hydrogenated amorphous silicon doped with boron.

3. A photoreceptor according to either of the above claims, further characterised in that the dielectric layer (33; 43; 55) comprises a nitride of silicon.

4. A photoreceptor according to claim 1 or 3, characterised in that the semiconductor is hydrogenated amorphous silicon.

5. Apparatus for etching or producing a semiconductor film on article surfaces, comprising an evacuable enclosure (79, 85, 93), means for evacuating the enclosure, electrode means (76a, 88a, 92), arranged to support an article (70a, 80a, 91) within the enclosure, means (74, 83, 96) for introducing into the evacuated enclosure a reactive or film forming gaseous material (G) at subatmospheric pressure, counter-electrode means (79, 85, 97) for applying an electric field to an article within the enclosure, when a power supply (180, 87, 102) is connected between the electrode means and the counter-electrode means, and means for controlling the pressure to maintain the negative glow region of a glow discharge adjacent the surface of the article, characterised in that the electrode means (76a, 88a, 92) are so arranged that the surface of an article (70a, 80a, 91) supported within the enclosure (79, 85, 93) by the electrode means is separated by a separation distance (S) from an electrode surface (71b, 81b, 91) placed into the enclosure, and in that the electrode surface is maintained at substantially the same potential as the electrode means, whereby a second negative glow region is maintained adjacent the electrode surface, and in that the separation distance (S) is sufficiently short that, when in use an electric field is applied between the electrode means and the electrode surface, and the counter-electrode means, the negative glow regions interact to reduce the voltage required to maintain the glow discharge from the value which would be required in the absence of the electrode surface.

6. Apparatus according to claim 5, characterised by electrode means (76a, 76b, 88a, 88b, 92) arranged to support a plurality of articles within the enclosure, and in that the electrode surface corresponding to each article is the surface of another article.

7. Apparatus according to claim 5 or 6, characterised in that the article is or the articles include a cylinder (70a, 70b), and further characterised by means (72a, 72b) for rotating the cylinder about its axis so that the surface of the cylinder may be uniformly etched or coated.

8. Apparatus according to 5 or 6, characterised in that the article or articles include planar members (80a, 80b, 91).

9. Apparatus according to any of claims 5 to 8, characterised by heating means (91a, 91b, 98) which maintain the temperature of the articles during depositing or etching, in a range so that the surface layer of the final article or articles has a high resistivity in the dark.

10. A method of etching or producing a film on a surface of an article (70a, 80a, 91) in an evacuable enclosure (79, 85, 93), in which the enclosure

is evacuated, a gaseous material (G) is introduced into the enclosure at subatmospheric pressure in the region of the articles, and an electric field is applied between a counter electrode (79, 85, 97) and the article, characterised by placing an electrode surface (71b, 81b, 91) into the enclosure to be separated by a separation distance (S) from the surface of the article, maintaining the electrode surface and the article at substantially the same potential, controlling the pressure to maintain negative glow regions of a glow discharge adjacent the surface of the article and the electrode surface, and setting the distance (S) to be sufficiently short that the negative glow regions interact to reduce the voltage required to maintain the glow discharge from the value which would be required in the absence of the electrode surface.

11. A method according to claim 10, characterised by placing a plurality of articles (70a, 70b, 80a, 80b, 91) into the enclosure (79, 85, 93) together, with the surfaces of adjacent articles being spaced by the separation distance (S), and electrically connecting the articles together, whereby the electrode surface corresponding to each article is the surface of another article.

12. A method according to claim 10 or 11, characterised by the step of heating the article or articles to be coated or etched.

13. A method according to claim 12, characterised by maintaining the temperature of the articles during depositing or etching, in a range so that the surface layer of the final article or articles has a high resistivity in the dark.

14. A method according to any of claims 10 to 13, characterised in that when the article is or the articles include a cylinder, the cylinder is rotated about its axis so that the surface of the cylinder may be uniformly etched or coated.

Patentansprüche

1. Auf der Oberfläche eines elektrisch leitenden Substrats angeordneter Photorezeptor, dadurch gekennzeichnet, daß eine erste Schicht (32; 42; 54) aus Halbleitermaterial auf der Oberfläche des Substrates (1), eine dielektrische Schicht (33; 43; 55) auf der Oberfläche der ersten Schicht aus halbleitendem Material und eine zweite Schicht (34; 44; 45; 56) aus Halbleitermaterial auf der Oberfläche der dielektrischen Schicht angeordnet sind und die Dicke der dielektrischen Schicht (33; 43; 55) hinreichend groß ist, um die Oberflächenspannung, die an die unbelichteten Flächen der Oberfläche der zweiten Schicht (34; 44; 45; 56) aus halbleitendem Material während der Aufladung durch Koronaentladung angelegt werden kann, über diejenige hinaus zu erhöhen, die an eine Schicht aus dem halbleitenden Material allein angelegt werden kann, sowie hinreichend klein ist, um die Ladung, die auf den Flächen der Oberfläche der zweiten Schicht aus halbleitendem Material zurückbleibt, wenn der Photorezeptor durch elektromagnetische Strahlung belichtet wird, zu verringern.

2. Photorezeptor gemäß Anspruch 1, dadurch gekennzeichnet, daß die erste Schicht (32; 42; 54) aus halbleitendem Material hydriertes, amorphes Silicium, das mit Bor dotiert ist, enthält.

3. Photorezeptor gemäß einem der obigen Ansprüche, dadurch gekennzeichnet, daß die dielektrische Schicht (33; 43; 55) ein Nitrid von Silicium enthält.

4. Photorezeptor gemäß Anspruch 1 oder 3, dadurch gekennzeichnet, daß der Halbleiter hydriertes, amorphes Silicium ist.

5. Vorrichtung zum Ätzen oder Herstellung eines Halbleiterüberzugs auf Oberflächen von Gegenständen mit einer evakuierbaren Umhüllung (79, 85, 93), Mitteln zum Evakuieren der Umhüllung, Elektrodenmitteln (76a, 88a, 92), die so angeordnet sind, daß sie einen Gegenstand (70a, 80a, 91) innerhalb der Umhüllung halten, Mitteln (74, 83, 96) zum Einführen eines reaktionsfähigen oder einen Überzug bildenden gasförmigen Materials (G) bei unteratmosphärischem Druck in die evakuierte Umhüllung, Gegenelektrodenmittel (79, 85, 97) zum Anlegen eines elektrischen Feldes an einen Gegenstand innerhalb der Umhüllung, wenn eine Stromquelle (180, 87, 102) zwischen die Elektrodenmittel und die Gegenelektrodenmittel geschaltet ist, sowie Mitteln zur Steuerung des Drucks, um den negativen Glimmbereich einer Glimmentladung an der Oberfläche des Gegenstandes aufrecht zu erhalten, dadurch gekennzeichnet, daß die Elektrodenmittel (76a, 88a, 92) derart angeordnet sind, daß die Oberfläche eines innerhalb der Umhüllung (79, 85, 93) durch die Elektrodenmittel gehaltenen Gegenstandes (70a, 80a, 91) von einer Elektrodenoberfläche (71b, 81b, 91), die in die Umhüllung eingebracht ist, durch eine Entfernung (S) getrennt ist, daß dies Elektrodenoberfläche auf praktisch demselben Potential wie die Elektrodenmittel gehalten wird, wodurch an der Elektrodenoberfläche ein zweiter negativer Glimmbereich aufrechterhalten wird, und daß die Entfernung (S) so kurz ist, daß, wenn im Betrieb ein elektrisches Feld zwischen den Elektrodenmitteln und der Elektrodenoberfläche sowie den Gegenelektrodenmitteln angelegt wird, die negativen Glimmbereiche derart zusammenwirken, daß sie die Spannung, die zur Aufrechterhaltung der Glimmentladung erforderlich ist, gegenüber dem Wert, der beim Fehlen der Elektrodenoberfläche erforderlich wäre, verringern.

6. Vorrichtung gemäß Anspruch 5, gekennzeichnet durch Elektrodenmittel (76a, 76b, 88a, 88b, 92), die derart angeordnet sind, daß sie eine Anzahl von Gegenständen innerhalb der Umhüllung halten, sowie dadurch, daß die zu jedem Gegenstand korrespondierende Elektrodenoberfläche die Oberfläche eines anderen Gegenstandes ist.

7. Vorrichtung gemäß Anspruch 5 oder 6, dadurch gekennzeichnet, daß der Gegenstand oder die Gegenstände einen Zylinder (70a, 70b) aufweist bzw. aufwiesen und daß Mittel (72a, 72b) zum Drehen des Zylinders um seine Achse vorgesehen sind, so daß die Oberfläche des Zylinders

gleichmäßig geätzt oder beschichtet werden kann.

8. Vorrichtung gemäß 5 oder 6, dadurch gekennzeichnet, daß der Gegenstand oder daß die Gegenstände planare Teile (80a, 80b, 91) aufweist bzw. aufweisen.

9. Vorrichtung gemäß einem der Ansprüche 5 bis 8, gekennzeichnet durch Erhitzungsmittel (91a, 91b, 98), die die Temperatur der Gegenstände während des Abschiedens oder Ätzens in einem derartigen Bereich halten, daß die Oberflächenschicht des fertigen Gegenstandes bzw. der fertigen Gegenstände einen hohen spezifischen Dunkelwiderstand aufweist.

10. Verfahren zum Ätzen oder Herstellen eines Überzugs auf einer Oberfläche eines Gegenstandes (70a, 80a, 91) in einer evakuierbaren Umhüllung (79, 85, 93), bei dem die Umhüllung evakuiert, ein gasförmiges Material (G) bei unteratmosphärischem Druck in dem Bereich der Gegenstände in die Umhüllung eingeführt und ein elektrisches Feld zwischen einer Gegenelektrode (79, 85, 97) und dem Gegenstand angelegt wird, dadurch gekennzeichnet, daß man eine Elektrodenoberfläche (71b, 81b, 91) derart in die Umhüllung einbringt, daß sie durch eine Entfernung (S) von der Oberfläche des Gegenstandes getrennt wird,

25 die Elektrodenoberfläche und den Gegenstand auf praktisch demselben Potential hält, den Druck derart steuert, daß negative Glimmbereiche einer Glimmentladung an der Oberfläche des Gegenstandes und der Elektrodenoberfläche aufrechterhalten werden, und die Entfernung (S) derart klein einstellt, daß die negativen Glimmbereiche

30 derart zusammenwirken, daß die Spannung, die zur Aufrechterhaltung der Glimmentladung erforderlich ist, im Vergleich zu dem Wert, der bei Abwesenheit der Elektrodenoberfläche erforderlich wäre, vermindert wird.

35 11. Verfahren gemäß Anspruch 10, dadurch gekennzeichnet, daß man eine Anzahl von Gegenständen (70a, 70b, 80a, 80b, 91) in die Umhüllung (79, 85, 93) zusammen einbringt, wobei die Oberflächen benachbarter Gegenstände durch die Entfernung (S) voneinander getrennt sind, und die Gegenstände zusammen elektrisch anschließt,

40 wodurch die zu jedem Gegenstand korrespondierende Elektrodenoberfläche die Oberfläche eines anderen Gegenstandes ist.

45 12. Verfahren gemäß Anspruch 10 oder 11, dadurch gekennzeichnet, daß man den oder die zu überziehenden oder zu ätzenden Gegenstand bzw. Gegenstände erhitzt.

50 13. Verfahren gemäß Anspruch 12, dadurch gekennzeichnet, daß man die Temperatur der Gegenstände während der Abscheidung oder des Ätzens in einem derartigen Bereich hält, daß die Oberflächenschicht des fertigen Gegenstandes bzw. der fertigen Gegenstände einen hohen spezifischen Dunkelwiderstand aufweist.

55 14. Verfahren gemäß einem der Ansprüche 10 bis 13, dadurch gekennzeichnet, daß in den Fällen, in denen der Gegenstand einen Zylinder darstellt oder enthält, der Zylinder um seine Achse gedreht wird, so daß die Oberfläche des

Zylinders gleichmäßig geätzt oder überzogen werden kann.

Revendications

1. Photorécepteur disposé sur la surface d'un substrat électriquement conducteur, caractérisé en ce qu'une première couche (32; 42; 54) d'un matériau semi-conducteur est disposée sur la surface du substrat (1), qu'une couche diélectrique (33; 43; 55) est disposée sur la surface de la première couche du matériau semi-conducteur, et qu'une seconde couche (34; 44; 45; 56) du matériau semi-conducteur est disposée sur la surface de la couche diélectrique, et que l'épaisseur de la couche diélectrique (33; 43; 55) est suffisamment importante pour accroître la tension superficielle qui peut être appliquée à des zones non éclairées de la surface de la seconde couche (34; 44; 45; 56) du matériau semi-conducteur pendant une charge par effet couronne, au-delà de ce qui peut être appliqué à une couche d'un matériau semi-conducteur seul, et est suffisamment petite pour réduire la charge subsistant dans des zones de la surface de la seconde couche du matériau semi-conducteur, lorsque le photorécepteur est éclairé par un rayonnement électromagnétique.

2. Photorécepteur selon la revendication 1, caractérisé en outre en ce que la première couche (32; 42; 54) du matériau semi-conducteur comporte du silicium amorphe hydrogéné dopé par du bore.

3. Photorécepteur selon l'une ou l'autre des revendications précédentes, caractérisé en outre en ce que la couche diélectrique (33; 43; 55) comporte du nitre de silicium.

4. Photorécepteur selon la revendication 1 ou 3, caractérisé en ce que le semi-conducteur est du silicium amorphe hydrogéné.

5. Appareil pour corroder ou produire une pellicule semi-conductrice sur des surfaces d'articles comprenant une enceinte (79, 85, 93), dans laquelle le vide peut être établi, des moyens pour établir le vide dans l'enceinte, des moyens en forme d'électrodes (76a, 88a, 92) agencés de manière à supporter un article (70a, 80a, 91) à l'intérieur de l'enceinte, des moyens (74, 83, 96) pour introduire dans l'enceinte, dans laquelle le vide a été établi, une substance gazeuse (G) réactive ou formant une pellicule, à une pression inférieure à la pression atmosphérique, des moyens en forme de contre-électrode (79, 85, 97) pour appliquer un champ électrique à un article situé dans l'enceinte, lorsque l'alimentation en énergie (180, 87, 102) est branchée entre les moyens en forme d'électrode, et les moyens en forme de contre-électrode, et des moyens pour commander la pression afin de maintenir une zone à incandescence négative d'une décharge à incandescence au voisinage de la surface de l'article, caractérisé en ce que les moyens en forme d'électrode (76a, 88a, 92) sont agencés de telle sorte que la surface d'un article (70a, 80a, 91) soit soutenue à l'intérieur de l'enceinte (79, 85, 93) par les moyens en forme d'électrode et séparée

d'une distance de séparation (S), d'une surface d'électrode (71b, 81b, 91) située dans l'enceinte, et en ce que la surface d'électrode est maintenue essentiellement au même potentiel que les moyens en forme d'électrode, ce qui a pour effet qu'une seconde région à incandescence négative est maintenue au voisinage de la surface d'électrode, et en ce que la distance de séparation (S) est suffisamment courte pour que, lorsqu'un champ électrique est appliqué, en cours d'utilisation, entre les moyens en forme d'électrode et la surface d'électrode, et les moyens en forme de contre-électrode, les régions à incandescence négative coopèrent pour réduire la tension requise pour maintenir la décharge à incandescence, à partir de la valeur qui serait nécessaire en l'absence de la surface d'électrode.

6. Appareil selon la revendication 5, caractérisé par des moyens en forme d'électrodes (76a, 76b, 88a, 88b, 92) agencés pour supporter une pluralité d'articles à l'intérieur de l'enceinte, et en ce que la surface d'électrode correspondant à chaque article est la surface d'un autre article.

7. Appareil selon la revendication 5 ou 6, caractérisé en ce que l'article est ou les articles contiennent un cylindre (70a, 70b), et en outre caractérisé par des moyens (72a, 72b) pour faire tourner le cylindre autour de son axe de sorte que la surface du cylindre peut être corrode ou recouverte d'une manière uniforme.

8. Appareil selon la revendication 5 ou 6, caractérisé en ce que le ou les articles incluent des éléments plats (80a, 80b, 91).

9. Appareil selon l'une quelconque des revendications 5 à 8, caractérisé par des moyens de chauffage (91, 91b, 98), qui maintiennent la température des articles, pendant le dépôt et la corrosion, dans une plage de valeurs telle que la couche de surface du ou des articles finaux possède une résistivité d'obscurité élevée.

10. Procédé pour corroder ou réaliser une pellicule sur une surface d'un article (70a, 80a, 91) dans une enceinte (79, 85, 93), dans laquelle le vide peut être établi, et selon lequel le vide est établi dans l'enceinte, une substance gazeuse (G) est introduite dans l'enceinte à une pression inférieure à la pression atmosphérique dans la zone des articles, et un champ électrique est appliqué entre une contre-électrode (79, 85, 97) et l'article, caractérisé par la mise en place d'une surface d'électrode (71b, 81b, 91) dans l'enceinte de manière qu'elle soit séparée de la surface de l'article par une distance de séparation (S), le maintien de la surface d'électrode et de l'article essentiellement au même potentiel, la commande de la pression de manière à maintenir des régions à incandescence négative d'une décharge à incandescence au voisinage de la surface de l'article et de la surface d'électrode, et réglage de la distance (S) à une valeur suffisamment courte pour que les régions à incandescence négative coopèrent de manière à réduire la tension requise pour maintenir la décharge à incandescence, à partir de la valeur qui serait requise en l'absence de la surface d'électrode.

11. Procédé selon la revendication 10, caractérisé par la mise en place d'une pluralité d'articles (70a, 70b, 80a, 80b, 91), ensemble dans l'enceinte (79, 85, 93), les surfaces d'articles voisins étant séparées par la distance de séparation (S), et le raccordement électrique des articles les uns aux autres, ce qui a pour effet que la surface d'électrode correspondant à chaque article est la surface d'un autre article.

12. Procédé selon la revendication 10 ou 11, caractérisé par l'étape opératoire consistant à chauffer le ou les articles devant être recouverts ou corrodés.

5

10

13. Procédé selon la revendication 12, caractérisé par le maintien de la température des articles pendant le dépôt ou la corrosion, dans une plage de valeurs telles que la couche superficielle du ou des articles finaux possède une résistivité d'abscurité élevée.

14. Procédé selon l'une quelconque des revendications 10 à 13, caractérisé en ce que, lorsque l'article est ou les articles incluent un cylindre, le cylindre est entraîné en rotation autour de son axe de sorte que la surface du cylindre peut être corrodée ou recouverte d'une manière uniforme.

15

20

25

30

35

40

45

50

55

60

65

0 070 715

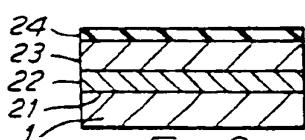
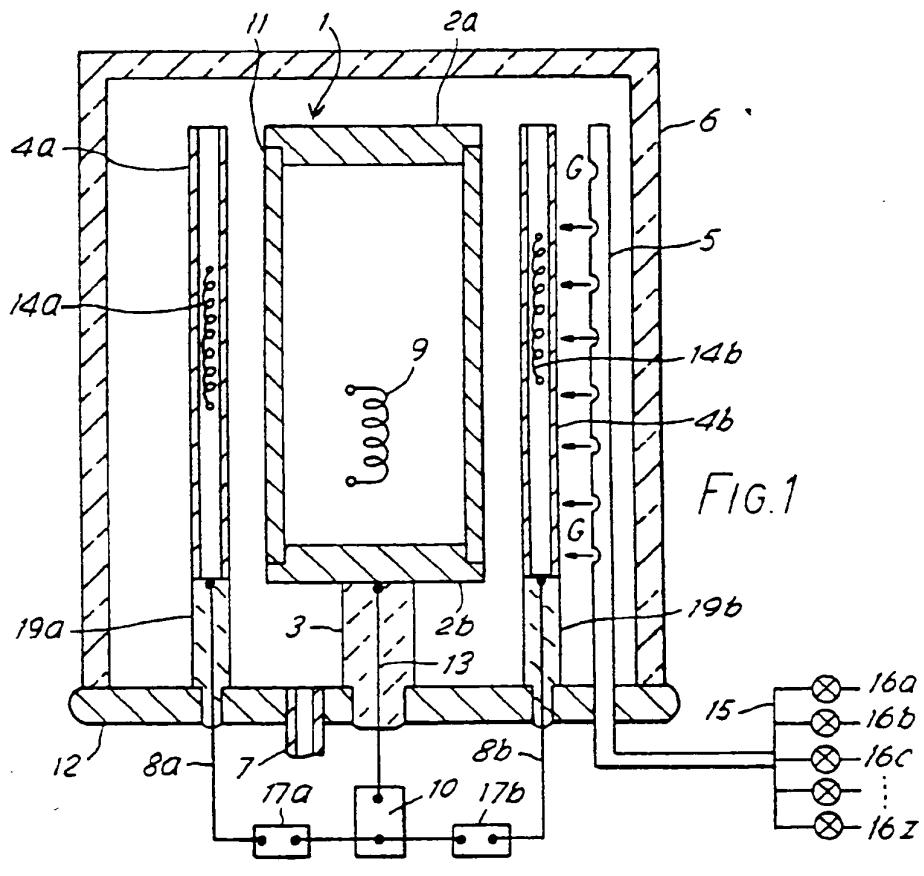


FIG. 2

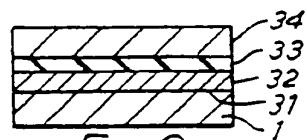


FIG. 3

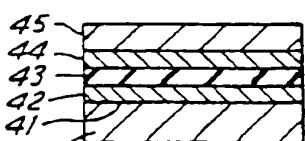


FIG. 4

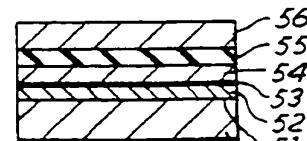
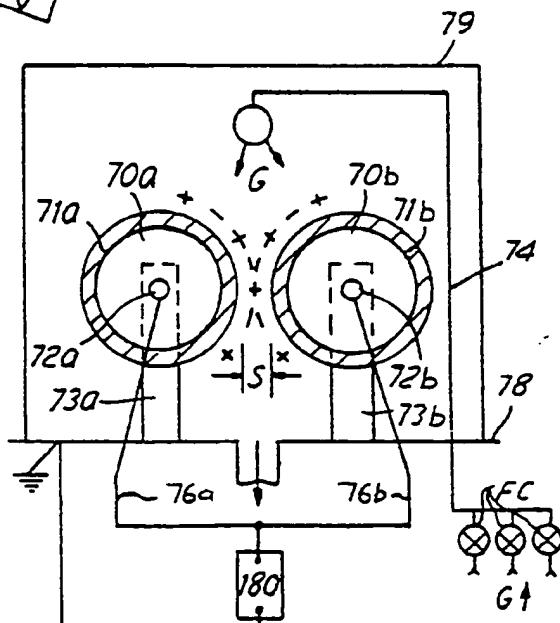
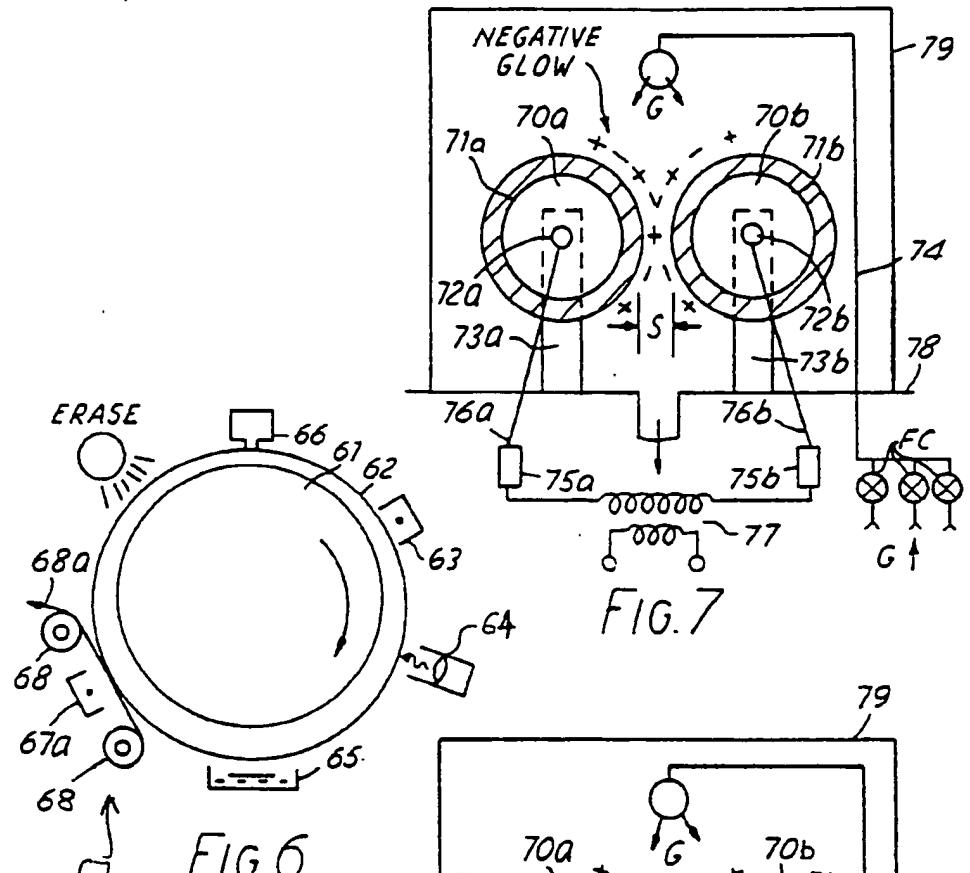


FIG. 5

0 070 715



0 070 715

